added nothing to the information supplied by the funnel and spray tests, and it was abandoned.

Other tests and observations made on fabrics which have been treated to increase the water resistance are briefly as follows:

Pin holes: The fabric is held before an electric light, and pin holes are rated as numerous, several, or none.

Condition of the dry fabric at —10° C., at ordinary room temperature and at 45° C. is rated as stiff, or supple, and as greasy, sticky, or rubs off.

Condition of the wet fabric is rated as stiff, or supple, and as greasy, sticky, or rubs off.

A reaction to litmus paper of the water extract is noted.

The sulfates are tested for.

Weight per square yard in ounces is determined before and after washing.

Threads per inch, warp and filling are counted.

Percentage of ash, qualitative tests for lead, zinc, copper, chromium, aluminum, and iron are determined when desirable.

Quantitative determination of copper is also made when put in mildew-proof fabrics.

An attempt is also made to determine the nature of the waterproofing material as well as the quantity present.

SUMMARY

The modified funnel test and the modified spray test when conducted under the standardized conditions described are simple of execution, give results within a reasonable time, and yield more information on the water resistance of cotton duck than the other tests which have been tried in the Bureau of Chemistry.

ADDENDUM

Since the presentation of this paper at the meeting of the AMERICAN CHEMICAL SOCIETY at Buffalo, April 7 to 11, 1919, there has appeared an article by Martin and Wood[1] entitled "Notes on the Quantitative Testing of Rainproof and Waterproof Cloth." These writers review briefly the various methods for determining the waterproof value of cloth, including the "drop test," "dash test," "trough or bag test," "filter test," "thistle tube test," and the Gawalouski apparatus. These methods, with the exception of the "drop test" and the "dash test" have already been reviewed in this paper. The "drip test" according to Martin and Wood is known as the "War Office test" and it is claimed that it is especially valuable, "in that it furnishes a fairly accurate numerical value of the degree of waterproofing."

The authors describe the "drop test" in which water is allowed to drip from a burette from a height of about 5 ft. at a rate of 20 drops per minute on to the fabric. The cloth is placed at an angle of 45° under which is laid a piece of white blotting paper. The dripping of water is continued until the water passes through the cloth and stains the blotting paper.

A similar test to this has been given a trial in this laboratory but it was discontinued for the spray test because it was believed the latter imitates much better the conditions of an actual rain. The drop test as described by Martin and Wood was, no doubt, devised for waterproofed garments and not for waterproofed cotton duck.

The "dash test" as described consists of holding the fabric horizontally and pouring water on it. Martin and Wood do not consider it of any particular value.

[1] *J. Soc. Chem. Ind.*, **38** (1919), 84-T.

UTILIZATION OF ASPHALTIC BASE ACID SLUDGE OBTAINED IN REFINING PETROLEUM AND SHALE OILS[1]

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At certain stages in the process of refining petroleum and shale oils after treatment with sulfuric acid the "acid sludge," as it is usually called, is cooked up by means of live steam, with concentrated sulfuric acid to separate any refinable oil retained by the usually pasty mass and to carbonize the remaining material. This is the common method of disposing of a residuum obtained in large amounts in oils especially of an asphaltic, or partially asphaltic base nature.

The process above outlined may be regarded as taking place in two stages, although they so merge one into the other that it, as practiced, appears as one. As the temperature of the mixture of acid sludge and acid is raised the retained oil escapes from the pasty mass, which becomes quite liquid with the elevation of temperature. The separated oil rises on top of the original mixture. This is effected within about an hour or an hour and a half. The raising of the temperature by means of steam is continued and the acid sludge and concentrated sulfuric acid are mixed intimately. This treatment is continued for several hours longer during which time the refuse or residuum (middle portion) becomes more or less decomposed and carbonized as shown by its change in character and the constant escape of sulfur dioxide, the latter being due to the reduction of sulfuric acid. On ceasing the agitation, the carbonized acid sludge and excess of concentrated acid used separate into two layers, the concentrated sulfuric acid being the bottom layer. The sulfuric acid is drawn from beneath to be used again, and the acid sludge thus produced is run out into a suitable conveyor trough and washed once with water, whereby usually about one-half of the retained acid is removed and is sometimes recovered. This washed, acid-cooked residue is usually burned with coal to get rid of it. It contains from 3 to 15 per cent of free sulfuric acid.

Many investigations have been carried out looking toward utilization of this cooked acid sludge, but the most economical practice to date appears to be its destruction by burning. Its production involves large and expensive lead-lined kettles and its disposition entails much labor. In fact, it is a nuisance to the refiner of petroleum. The products of the combustion are unusually rich in sulfur dioxide.

It has been determined that this expensive treatment is unnecessary and furthermore that the acid sludge, if obtained from an oil with an asphaltic, or partially asphaltic base, may be converted almost directly into a product of commercial value.

[1] Presented at the 57th Meeting, American Chemical Society, Buffalo, N. Y., April 2 to 7, 1919.

If samples are taken during the preliminary heating of the mixture referred to above, it may be observed when the major portion of the further refinable oil has separated. That condition obtains usually within the first hour or hour and a half, that is to say, at the end of the first stage when actual carbonization is near the minimum. Three layers form. The oil separates on top as indicated, and the excess concentrated acid accumulates at the bottom. The top layer is drawn off. The middle portion, which has not been heated high enough and long enough in contact with the concentrated acid to become carbonized and have its asphaltic nature destroyed, is a pasty mass, quite liquid at the temperature attained, and contains from 15 to 25 per cent (or even more) sulfuric acid. It is drawn off and is given one washing (1 : 5) with water. The diluted acid liquor is drawn off and sent to the concentrator. The asphaltic mass, in weighed portions, is run at once into a suitable mill, where it is mixed with the proper proportion (as determined by rapid analysis), usually in slight excess, of lime which has been freshly slaked with sufficient water to cause it to crumble into a powder. The mixture is then kneaded in the mill. Much heat is generated by the union of the free acid and calcium hydroxide, but not enough to char the material. If sufficient heat has not been generated during the mixing to render the mass fluid (due to low acid content), it may be heated to about 220° C., when as a fluid it may be run into a suitable receptacle for marketing. Finely divided limestone may be substituted for the slaked lime powder.

The asphaltic or bitumenic material present in the residuum has not been destroyed but simply incorporated with some 10 to 40 per cent of calcium sulfate, depending upon the amount of free acid present in the washed acid sludge.[1] The asphaltic or bitumenic material present may be readily extracted by the solvents generally used for dissolving those substances.

The whole mass exhibits the properties associated with asphalt, modified, of course, by the calcium salt produced. It becomes fluid when sufficiently heated and may be applied to metal, masonry, wood, etc. It adheres well and, from 6 months' test, is impervious to water. It mixes with rosin and other substances added to asphalt for particular purposes.

CONCLUSION

A by-product, formerly a nuisance, costing money to get rid of it, has been converted into a useful material possessing a commercial value.

REACTIONS OF ACCELERATORS DURING VULCANIZATION[2]

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The highest powered organic accelerators known to-day are the carbon bisulfide reaction products of strong organic bases. Perhaps the best example is the piperidine salt of piperidyl-dithiocarbamic acid. The formation of this compound is shown by the following equations:

$$C_5H_{10}{=}NH + CS_2 \longrightarrow C_5H_{10}{=}N{-}\underset{\displaystyle S-H}{\overset{\displaystyle |}{C}}{=}S$$

Piperidine — Piperidyl-dithiocarbamic acid

$$C_5H_{10}{=}N{-}\underset{\displaystyle H-S}{\overset{\displaystyle |}{C}}{=}S + C_5H_{10}{=}NH \longrightarrow C_5H_{10}{=}N{-}\underset{\displaystyle H}{\overset{\displaystyle S}{\overset{\displaystyle |}{C}}}{=}S \cdot \underset{\displaystyle H}{N} = C_5H_{10}$$

Piperidine salt of piperidyl-dithiocarbamic acid

Due to the strong basic nature of piperidine, this salt is stable and may be isolated as such. Strong aliphatic bases such as dimethylamine also give stable dithiocarbamates which are very powerful accelerators.

Thiocarbanilide, which is perhaps the most widely used commercial accelerator, is formed by the same mechanism of reaction, there first being formed the aniline salt of phenyl-dithiocarbamic acid,

$$C_6H_5{-}NH_2 + CS_2 \longrightarrow C_6H_5{-}\overset{\displaystyle H}{N}{-}\underset{\displaystyle S-H}{\overset{\displaystyle |}{C}}{=}S$$

$$C_6H_5{-}\overset{\displaystyle H}{N}{-}\underset{\displaystyle S-H}{\overset{\displaystyle |}{C}}{=}S + C_6H_5{-}NH_2 \longrightarrow C_6H_5{-}\overset{\displaystyle H}{N}{-}\underset{\displaystyle H}{\overset{\displaystyle S}{\overset{\displaystyle |}{C}}}{=}S \cdot \underset{\displaystyle H_2}{N}{-}C_6H_5.$$

This aniline salt is extremely unstable due to the weak basic properties of aniline and cannot be isolated as such. The ammonium salt of this phenyl-dithiocarbamic acid may be isolated but decomposes on standing. The metallic salts of dithiocarbamic acids are much more stable according to Krulla.[1] The aniline salt, by loss of hydrogen sulfide, produces thiocarbanilide,

$$C_6H_5{-}\overset{\displaystyle H}{N}{-}\underset{\displaystyle H}{\overset{\displaystyle S}{\overset{\displaystyle |}{C}}}{=}S \cdot \underset{\displaystyle H_2}{N}{-}C_6H_5 \longrightarrow \underset{\displaystyle C_6H_5-NH}{\overset{\displaystyle C_6H_5-NH}{\overset{\displaystyle |}{\underset{\displaystyle |}{C}}}}{=}S + H_2S.$$

The stable dithiocarbamates above mentioned lose hydrogen sulfide in a similar manner when heated to the temperatures used in the vulcanization of rubber and produce thiourea derivatives. It is, therefore, quite possible that they may function as curing agents in the same manner as thiocarbanilide.

André Dubosc[2] has stated that thiourea derivatives can "furnish in a colloidal state all the sulfur necessary for vulcanization." In checking up this statement it appeared at first that Dubosc was correct, but the cures obtained were soon shown to be due to free sulfur present as an impurity in the accelera-

[1] The process is covered by U. S. Patent 1,234,985, July 1917.

[2] Presented before the Rubber Division at the 58th Meeting of the American Chemical Society, Philadelphia, Pa., September 2 to 6, 1919.

[1] *Ber.*, **46**, 2669.

[2] *India Rubber World*, February 1, 1919.